

## Novel time-temperature and 'consume-within' indicator based on gas-diffusion

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# Novel time-temperature and 'consume-within' indicator based on gas-diffusion

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**The novel time-temperature indicator label comprises an ammonia sensitive indicator layer film pressed onto a second film, comprising an ammonia-generating, adhesive layer. When separated the blue-coloured indicator film reverts back to its original (ammonia free) yellow form at a controllable, temperature dependant rate. The labels are easily made and stored.**

The use of indicators to provide useful information about the quality of the packaged food during transport and storage is central to intelligent or smart packaging<sup>1</sup>. Smart packaging is a growing area of research and commercialisation and there are a number of notable review articles and books<sup>1-7</sup>. Common analytes include: oxygen<sup>6</sup>, carbon dioxide<sup>8</sup>, ammonia/ammonia<sup>9,10</sup> and temperature<sup>11</sup>.

Temperature is one of the primary controllers of the rates of food spoilage through various degradation pathways, including: microbial growth and enzyme and non-enzyme based oxidation reactions<sup>12</sup>. It is not surprising, therefore, that time-temperature indicators, TTIs, are playing an increasingly important role in food packaging, especially in the distribution chain of chilled and frozen goods<sup>12-17</sup>. A TTI shows an easily observed, time-temperature dependent change that reflects the temperature history of the temperature-sensitive product to which it is attached<sup>12,13</sup>. For example, the MonitorMark™ TTI<sup>14</sup>, manufactured by 3M, comprises a blue dye in a fatty ester which melts at a defined threshold temperature and then diffuses along the wick at a temperature dependant rate. This type of TTI is routinely used to monitor the thermal exposure of pallets of temperature sensitive products, including many foods, vaccines and drugs. In contrast, the Fresh-Check® Freshness, 'You can See™' label<sup>15</sup>, is based on a temperature-dependant polymerisation which causes the label to darken with time and is used on individual packaged foods, to identify those that have not been refrigerated correctly and

so are not fresh. Other chill or frozen chain TTI monitors include: OnVu™ 16 (notable for being UV activated), from Bizerba GmbH, and Timestrip™, from Timestrip™ (like MonitorMark™ – a liquid diffusion based indicator). In many cases (e.g. MonitorMark™ and Timestrip™) the TTI is activated by breaking a seal, whereas others, so called 'full-history' TTIs, like Fresh-Check™<sup>15</sup>, are always active, and so need to be made and stored below their threshold temperature. The main barrier to the widespread use of TTIs on individual packages in the chill or frozen chain is cost, with MonitorMark™ and Timestrip™ indicators typically costing > \$1 ea<sup>14,17</sup>, making them often too expensive for use with individual commercial packages. The printable Fresh-Check® indicator is much cheaper<sup>15</sup>, but even when 1-2 million indicators are produced, their cost is still > \$0.05 ea.<sup>18</sup>, which, for the food packaging industry at least, is usually considered too expensive for use with individual packages. In addition, the latter labels need to be stored frozen, which adds to the cost of their production, distribution and application<sup>13,15</sup>. This communication describes an alternative TTI label, that is: readily stored at ambient temperature, inexpensive to produce, easily activated, and which works via a mechanism that is completely new to TTI technology.

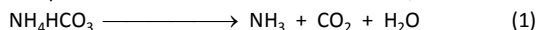
The label comprises an ammonia-sensitive indicator layer film pressed onto a second film, comprising an ammonia-generating, adhesive layer. The ammonia-sensitive indicator layer was created using an ink containing: 27 mg of the dye bromophenol blue, BPB, dissolved in 0.95 g of methanol and 6.4 g of ethanol. To this were added 0.5 g of the polymer, polyvinyl butyral, PVB, and 0.5 g of the plasticiser, tributyl phosphate, TBP. The BPB ink was applied onto a 45 µm thick poly(ethylene terephthalate), PET, substrate using a draw-down method and a K-bar No. 8, to give a dry, yellow-coloured film, with a thickness of ca. 8 µm, as measured by SEM (see figure S1 in the Electronic Supplementary Information, ESI). The formulation of the ammonia-sensitive indicator can be summarised as: PVB/BPB/TBP in which the components were present in the ratio: 100/2.7/100 parts-per-hundred resin, pphr, respectively. The ammonia-generating layer was made

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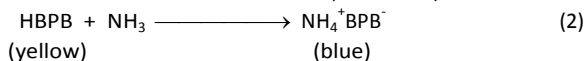
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using an ink containing: 2.0 g of ammonium bicarbonate dissolved in 10 g of water, to which were added 10 g of the pressure-sensitive, water-based adhesive Tackwhite AP03 HP (50% solids; Adhesive Technical Services). This ammonia-generating adhesive was coated onto a 45  $\mu\text{m}$  thick PET film using a K bar number 5, to yield a tacky dry coat with a thickness of 5  $\mu\text{m}$  (see figure S2 in the *ESI*) and a component ratio, in pphr, of 100/40 for the formulation; Tackwhite AP03 HP/ $\text{NH}_4\text{HCO}_3$ .

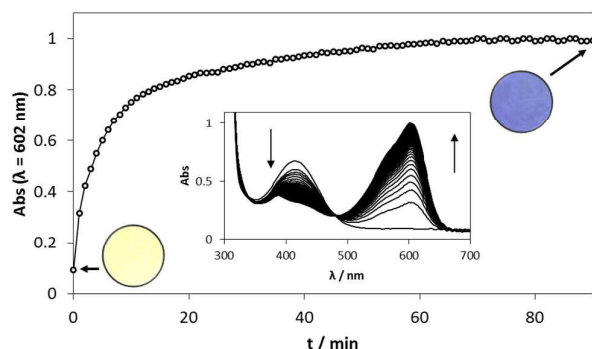
Upon pressing the two films together to create the label, which we shall refer to as the 'charging step', the initial yellow colour of the indicator film changes to blue, as the ammonia, generated by the gradual decomposition of the ammonium bicarbonate, i.e.



diffuses into the indicator film and reacts with the yellow protonated form of the BPB indicator, i.e. HBPB, as follows:



to form the blue coloured ammonium ion pair of the deprotonated form of BPB, i.e.  $\text{NH}_4^+\text{BPB}^-$ . A typical set of UV/vis absorption spectra of the indicator film, recorded as a function of time, upon pressing the two layers together to form the label, are illustrated in figure 1 (inset diagram), along with photographs of the label taken before and at the end of this process, and a plot of the absorbance at  $\lambda(\text{max})$ , = 602 nm, for the deprotonated form of BPB, i.e.  $\text{NH}_4^+\text{BPB}^-$ , as a function of time after pressing the two films together.

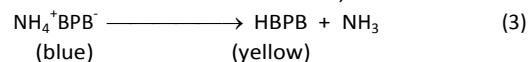


**Figure 1:** Time vs. absorbance data (at 602 nm) recorded for a 100/2.7/100 BVP/BPB/TBP TTI film in its charging stage at 22 °C. The inset diagram and photographs illustrate the UV-vis spectral changes and colour changes exhibited by the label as a function of time.

Further work showed that the charging step is ca. 25 times longer in duration if the plasticiser is omitted from the formulation of the indicator layer, as the plasticiser aids gas diffusion through the indicator film. The blue-coloured, charged label exhibited a good shelf-life, in that it shows no change in colour, or response time, when stored for over six months under ambient, dark conditions. Although the label was not designed specifically for re-use; additional experiments showed that it could be used at least 2 times over, with the same ammonia-generating, adhesive layer, and > 5 times over, using a new adhesive layer each time, and each

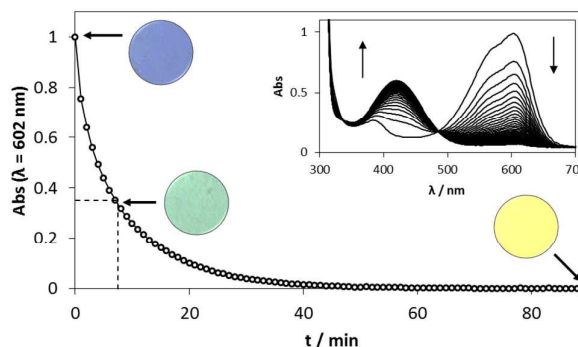
time without exhibiting any noticeable change in response characteristics.

The label is 'activated', by peeling off the top (ammonia-generating) adhesive layer, so as to reveal the 'naked' ammonia-charged, blue coloured indicator film. As a consequence of this action, the indicator film then slowly changes in colour to its original yellow-coloured form due to the diffusion of the ammonia out of the film, i.e.



Crucially, the rate of this colour change, i.e. reaction (3) is temperature dependent.

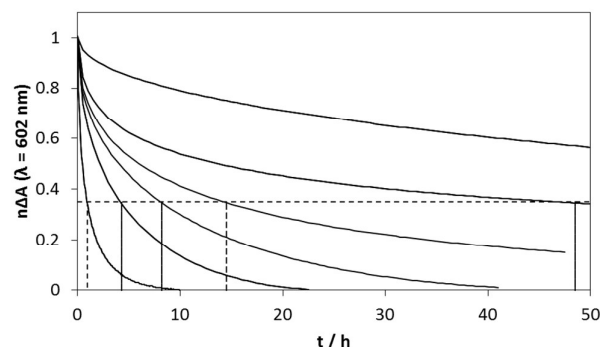
A typical set of UV/vis absorption spectra of the indicator film, recorded as a function of time, upon activation of the charged label, are illustrated in figure 2 (inset diagram), along with a selection of photographs of the label taken at the same time and a plot of the absorbance at  $\lambda(\text{max})$  for  $\text{NH}_4^+\text{BPB}$ , as a function of time after 'activation', i.e. peeling off the top layer. Thus, at room temperature, the time taken for the film to turn from blue to green, when it had recovered 65% of its original yellow colour,  $t(\text{green})$ , is ca. 8 min, and ca. 45 min to recover fully (i.e. turn from blue to yellow). Note also that, at room temperature, in the absence of the plasticiser,  $t(\text{green})$  is ca. 380 min and takes ca 48 h to recover its colour fully; thus, the recovery time of the indicator can be controlled via the level of plasticiser used to formulate the film.



**Figure 2:** Time vs. absorbance data (at 602 nm) recorded for a 100/2.7/100 BVP/BPB/TBP TTI film in its activation stage at 22 °C. The inset diagram and photographs illustrate the UV-vis spectral changes and colour changes exhibited by the label as a function of time.

The parameter,  $t(\text{green})$ , is employed here as a temperature dependent, threshold time that characterises the indicator film's response. Thus, given the suggested temperature of a household fridge is 5 °C, then, ideally,  $t(\text{green})$  should be ca. 48 h, at ca. 5 °C, since this is the recommended time period during which most fresh (i.e. no preservatives), refrigerated food, in an opened package, should be consumed. In this role, the indicator would function not only as a TTI, but also as a 'consume within' indicator for fresh food, in which if the indicator film was any shade between blue and green, the food would be still safe to eat, but not, if it appeared more yellow than green.

Unfortunately, as noted earlier, the 100/2.7/100 BVP/BPB/TBP TTI film illustrated in figure 2, exhibited a  $t(\text{green})$  value of ca. 8 min at 22 °C and, at 5 °C, this is only extended to 150 min. However, as noted above, by decreasing the level of plasticiser present, it is possible to increase the value of  $t(\text{green})$ . A quick study of this effect revealed that by using 10 times less plasticiser, i.e. 10 phr of TBP, rather than 100 phr, a  $t(\text{green})$  value of ca. 48 h can be achieved for a charged 100/2.7/10 BVP/BPB/TBP indicator film at 5 °C. The absorbance (at 602 nm) decay profiles were determined for such a 100/2.7/10 BVP/BPB/TBP indicator film as a function of temperatures and the results are illustrated in figure 3 below.



**Figure 3:** Normalised absorbance,  $n\Delta A$ , (at 602 nm) decay profiles recorded for a charged 100/2.7/10 BVP/BPB/TBP indicator film at the following temperatures (from left-to-right): 22 °C, 15 °C, 10 °C, 7.5 °C, 5 °C, and 2 °C. The broken horizontal line identifies the different values of  $t(\text{green})$ , when  $n\Delta A = 0.35$ , for the different temperatures.

The values of  $t(\text{green})$ , determined using the data in figure 3, were then used to generate an Arrhenius plot, from which an activation energy of  $157 \pm 17 \text{ kJ mol}^{-1}$  for the 100/2.7/10 BVP/BPB/TBP indicator film, was calculated.

Specific food degradation processes that exhibit an activation energy similar to that of the activated indicator, i.e.  $157 \pm 17 \text{ kJ mol}^{-1}$ , include those associated with salads and fruit, i.e. ascorbic acid degradation, non-enzymic browning, anthocyanin degradation and chlorophyll degradation<sup>19</sup>. In addition, a common microbial mechanism associated with the spoilage of beef, involving lactic acid bacteria, has a similar, activation energy<sup>19</sup>. Thus, the 100/2.7/10 BVP/BPB/TBP label has potential as a 'consume-within' indicator for refrigerated salads, fruit and some meat, like beef. Thus, Figure 4 demonstrates the possible use of this type of label as a 'consume within' indicator on a refrigerated at 5 °C, opened pack of beef, which should be consumed within 48 h. Note that up to a period of 48 h, at 5 °C, the indicator is still blue/green, but after this time it has turned yellow, indicating that the food is no longer fresh. By varying the plasticiser level, it is possible to make 1 day and 3 day 'consume-within' TTIs, for other fresh foods, such as fish and cooked meats, respectively.



**Figure 4** Photographs of an opened package containing beef, refrigerated at 5 °C with the 'consume within' indicator after: 0, 48 and 72 h.

Although the use of ammonia as the gas to activate the indicator might appear to be a concern, the indicator is small (ca. 3 cm<sup>2</sup>) and thin (8 μm) and calculations show that the ammonia it would release into the atmosphere of the fridge (0.5 m<sup>3</sup>) is negligible when compared to the daily exposure limit (ca. 1000 times below) and over 1600 times below that detectable by smell. Another possible concern is whether the intrinsic ammonia ammine exuded by the meat, as it spoils, will set-off the sensor response. However, this is unlikely, since the ammonia indicator used was made purposely so as to be not very sensitive towards ammonia; i.e. a 50% change in colour is produced by ca. 60 ppmv of ammonia, which is 12 times higher than the level that can be detected by humans. Thus, even if the food decay was sufficient to generate a level of ammonia that was easily detected by smell, this would be at a level that was high enough as to affect the indicator. Evidence for this was provided the results of experiments conducted using the label on packaged beef, see figure 4, since in all this work the sensor was unaffected by the deterioration of the meat, even long after 72 h, when the meat began to smell noticeably.

A 'consume within' indicator would help support the significant, current effort to reduce household food waste, much of which is still safe to eat, but is thrown away largely because the consumer is unsure about its edibility<sup>20</sup>. A consume-within TTI, as described here would help reassure the consumer that the food in an opened, refrigerated package has not exceeded the usual two day 'consume within' window, as recommended by many food product suppliers.

A new type of TTI label is described, based on an analyte gas (in this case ammonia) diffusing into an indicator film, which is referred to as the 'charging' step. Upon peeling off the top colourless, (charging) layer, referred to as the 'activation step',

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the analyte gas diffuses out of the indicator film at a rate that is temperature dependent. This is a new, simple, inexpensive approach to making a TTI that is readily stored under ambient conditions for > 6 months. The TTI response time of the label can be controlled by varying the level of plasticiser used in the formulation of the indicator layer, so that a 48 h, 'consume-within' TTI is made that functions at 5 °C, with an activation energy similar to that of the spoilage processes for refrigerated salads, fruit and beef. Ultimately, this TTI could play a significant role in reducing the overall burden of household food waste on the environment, by reducing the significant amount of food that is thrown away while still safe to eat due to a lack of reassurance regarding the latter, since the latter could be provided by the TTI.

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